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(54) Polyglycolic acid manufacture

(57) A process for the preparation of polyglycolic acid is provided. The process comprises reacting in one step formaldehyde and carbon monoxide in the presence, as catalyst, of an effective amount of a methanesulphonic acid. Preferred methanesulphonic acids are methanesulphonic acid itself and trifluoromethanesulphonic acid.

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SPECIFICATION

Polyglycolic acid manufacture

The present invention relates to a process for the preparation of polymers of polygcolic acid, $HOCH_2CO_2H$, termed polyglycolic acids. In particular the invention relates to the preparation of polyglycolic acids, having a formula $HO(CH_2CO)_nOH$ where n is an integer and a molecular weight in excess of 600, in a single stage reaction using formaldehyde and carbon monoxide as reactants.

Glycolic acid can be prepared by the carbonylation of formaldehyde in the presence of sulphuric acid (DT 2652-003), hydrogen fluoride (US 4,228,305) or an acid ion exchange resin (J5 6073-042) as a catalyst. The reaction, which is carried out at elevated temperature and pressure, produces the glycolic acid in high yield with no more than trace amounts of polymeric side-products.

Processes which describe the formation of polyglycolic acid as an intermediate from formaldehyde and carbon monoxide have been described in US 4,188,494 and DE 3,144,794. The references describe the use of e.g. chlorosulphonic acid, boron trifluride, hydrogen fluoride and dimethyl sulphate as catalysts.

It has now been found, however, that polyglycolic acid can be produced in high yields by using methane sulphonic acid as a catalyst in the above reaction. By producing polyglycolic acid in one step from formaldehyde and carbon monoxide, the extra processing step of polymerising the glycolic acid is obviated.

Accordingly, the present invention provides a process for the production of polyglycolic acid from formaldehyde and carbon monoxide, which process comprises reacting the formaldehyde with the carbon monoxide at elevated temperature and pressure characterised in that the reaction is carried out in the presence of, as catalyst, an effective amount of a methanesulphonic acid.

Any source of formaldehyde can be used as a reactant providing it is water free. Examples of suitable sources include formalin and paraformaldehyde, trioxin, and gaseous formaldehyde of which paraformaldehyde is preferred.

Similarily, any carbon monoxide source including pure carbon monoxide or mixtures of carbon monoxide and gases such as nitrogen, hydrogen, carbon dioxide and any other gases which are inert under the reaction conditions can be used.

The carbonylation is carried out in the presence of a methanesulphonic acid as a catalyst. The methanesulphonic acid is preferably either unsubstituted methanesulphonic acid itself, or trifluoromethanesulphonic acid. In general it is preferred to add the methanesulphonic acid catalyst in amounts up to 50 % by weight of the reaction mixture.

The reaction is carried out at elevated temperature and pressure. The preferred ranges of temperature and pressure are 40-150°C and 10 to 200 bar respectively.

The reaction described above is preferably carried out in the liquid phase. The liquid medium is created by the addition of an inert solvent. The inert solvent is preferably one which is easily separable from the polyglycolic acid product at the end of the reaction. Preferred solvents include halobenzenes, for example chlorobenzene, bromobenzene and other polar solvents which are unreactive under the reaction conditions.

The polyglycolic acid can, if desired, by hydrolysed to glycolic acid in a subsequent step.

The reaction may be carried out either batchwise or continuously and is illustrated by the following Example.

Example

30 g of paraformaldehyde, 30 g of chlorobenzene and 32.5 ml of methanesulphonic acid catalyst were charged to a 30 ml stainless steel autoclave. The autoclave was sealed and heated to 80°C under 68 bar of carbon monoxide. After 15 minutes reaction the mixture was cooled and the contents of the autoclave analysed. 166 g of polyglycolic acid were separated from the product mixture by filtration.

CLAIMS

1. A process for the production of polyglycolic acid from formaldehyde and carbon monoxide which process comprises reacting the formaldehyde with the carbon monoxide at elevated temperature and pressure characterised in that the reaction is carried out in the presence of, as catalyst, an effective amount of a methanesulphonic acid.

2. A process as claimed in claim 1 characterised in that the methanesulphonic acid is unsubstituted methanesulphonic acid.

3. A process as claimed in claim 1 characterised in that the methanesulphonic acid is triflormethanesulphonic.

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